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A THESIS

THE AREA AND ORIENTATION OF MOLECULES ADSORBED ON CHARCOAL

by

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THE AREA AND ORIENTATION OF
MOLECULES ADSORBED ON
CHARCOAL

Professor

Professor

Professor

THE AREAS AND ORIENTATION OF MOLECULES ADSORBED ON CHARCOAL

Submitted in partial Fulfillment
of the
Requirements for the Degree of
Master of Science

by

D. M. Miller, B.Sc.

Under the Direction of
Dr. J. L. Morrison

Time Devoted to this Work - 7 Months

Edmonton, Alberta. April, 1946

The author wishes to express his appreciation to all who have assisted in the completion of this work:

To Dr. Morrison under whose guidance this project was undertaken and whose generous advice and assistance has enabled the project to be completed.

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HISTORICAL INTRODUCTION - GENERAL

HISTORICAL INTRODUCTION
- GENERAL -

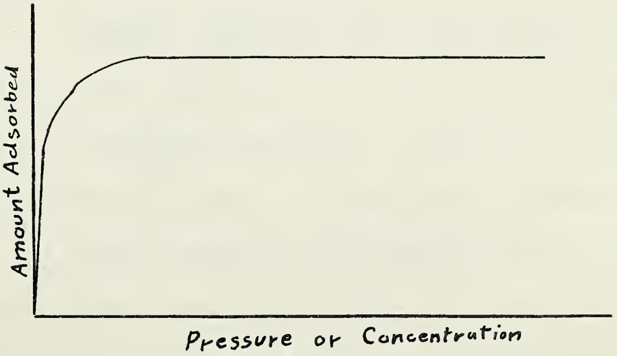
The purpose of this work is to determine the surface areas of charcoals of different degrees of activation by the adsorption of organic acids from aqueous solutions and by the adsorption of butane and nitrogen; and conversely, to use charcoals of different degrees of activation as a tool to elucidate the relation between adsorption and the molecular structures of organic acids and other molecules.

Various methods for determining the surface areas of porous materials have been proposed. Probably the most effective of these is calculation of the area from determinations of the maximum amounts of solutes adsorbed from solution, or of gases adsorbed on the surface of the solid. While this method may not yield the total surface, it provides us with a measure of the surface accessible to these molecules, an important consideration in Chemistry.

Adsorption may be one or both of two types, physical adsorption, in which the adsorbed layer is held by Van der Waal's forces, and chemical adsorption, in which it is held by chemical bonds. The type encountered in this work is physical adsorption.

The amount of physical adsorption has been found to be a function of the temperature, pressure and the nature of adsorbate and adsorbent. In determining surface areas, usually only the pressure (in the case of gases) or concentration (in the case of solutions) is altered. A graph of the amount adsorbed per unit weight of adsorbent against the pressure or concentration results in a curve known as an isotherm.

These isotherms may assume various shapes dependent on the type of adsorption. Charcoal generally exhibits the simplest of these. It rises sharply at first and gradually becomes parallel to the pressure axis as the pressure is extended, (see below).



This type of adsorption has been given the most successful interpretation by Langmuir (1), who

proposed an equation based on unimolecular adsorption: -

$$y = \frac{p\ b\ n}{1 + p\ n}$$

Where y is the quantity of substance adsorbed per gram adsorbent, p is the pressure (or concentration) and n and b are constants which hold for a given system. This equation may be resolved into an equation for a straight line, thus:

$$\frac{p}{y} = \frac{1}{b\ n} + \frac{p}{b}$$

The maximum amount adsorbed can be calculated from the inverse slope of the graph of P/y against P.

Emmett, Brunauer and Teller (2) have extended this principle to all types of isotherms and have developed equations applying to multimolecular adsorption and capillary condensation.

Many workers have measured surface areas by adsorption from solutions, the most popular adsorbates being the lower fatty acids and alcohols.

Paneth and Radu (3), finding that dyestuffs adsorbed in a unimolecular layer on diamond, assumed

that this also applied to charcoals, and determined the areas of charcoals by adsorption of dyestuffs, lead nitrate and acetone in aqueous solutions. They attributed the wide variations in areas found to the screening effect of small pores.

Garner, McKie and Knight (4) offer the following criteria in choosing adsorbates for measurements of areas of porous materials:

(1) the longest molecular dimension should be smaller than the radius of the smallest capillary in the porous body,

(2) the molecule should be capable of packing easily in the surface and in such a manner that the lateral forces between the adsorbed molecules increase the stability of the film,

(3) the adsorbed molecules should be so oriented on the surface that the exposed groups of the molecules of the first layer exert weak subsiduary valency forces on the second layers, thus reducing the tendancy to form multilayers. On the basis of these criteria, Lemieux and Morrison (5) chose aqueous solutions of short chain fatty acids to determine the surface areas of charcoals.

Linner and Gortner (6) measured the adsorption of various acids on norite in an attempt to

correlate molecular structure and adsorbability. They concluded that branching of the hydrocarbon chain has little effect on total adsorption but that an increase in the number of carboxyl groups decreases adsorption. The relative adsorption areas of the acids were computed, based on the value of 21 $Å^2$ for acetic acid. None of these experiments was carried out to saturation adsorption, however, and they suggest that a more valid method for determining the effect of molecular structure is to compare the adsorption values obtained for a saturated solution.

The present work is a continuation of the investigation started by Lemieux and Morrison (5). The series of charcoals used here is the same as the one employed by them with the exception of Charcoal 8, of which the supply was inadequate. The adsorbates they used were acetic, propionic, butyric, valeric and benzoic acids, while the additional acids employed here were caproic, isobutyric, isovaleric, trimethylacetic, crotonic, oxalic, malonic, succinic, glutaric, adipic, fumaric and maleic. Further, adsorption isotherms for butane and nitrogen were measured.

The work of Lemieux and Morrison has indicated unimolecularity of adsorption and has

given much information as to the porosity of the samples.

Trost and Morrison (7) investigated the effect of overactivation and found that it was accompanied by a decrease in surface area.

Kisselev and Shcherbakova (8), working with organic acids and alcohols and a single charcoal, attempted to show that the adsorbate is forced out of solution filling the pores of the adsorbent. An attempt is made in the present work to reconcile their experimental results with those of Lemieux and Morrison, at the same time indicating a fundamental difference in interpretation.

EXPERIMENTAL

EXPERIMENTAL

Materials: - The materials employed in this work were:

Caproic acid, C.P., Fisher Scientific Company

Isobutyric acid, Eastman Kodak Company

Isovaleric acid, Eastman Kodak Company

Trimethylacetic acid, Eastman Kodak Company

Crotonic acid, practical grade recrystallized, Eastman Kodak Company

Oxalic acid, technical grade recrystallized, Central Scientific Company

Malonic acid, Eastman Kodak Company

Adipic acid, British Drug Houses Limited

Succinic acid, Eastman Kodak Company

Fumaric acid, practical grade recrystallized, Eastman Kodak Company

Maleic acid, recrystallized, British Drug Houses Limited

Potassium acid Phthalate, reagent, Merik & Company, Inc.

Helium gas, Ohio Chemical and Mfg. Co.

Butane gas, C.P., Ohio Chemical and Mfg. Co.

Trimethylene bromide, technical, Eastman Kodak Company

Glutaric acid was not available but was prepared from trimethylene bromide by the hydrolysis

of its cyanide (9). The nitrogen used was tank nitrogen purified by passage over red hot active copper, phosphorous pentoxide and soda lime.

As stated above, the same series of charcoals was employed here as that used by Lemieux and Morrison with the exception of number 8 of which the supply was inadequate. The data supplied with these charcoals is given in table I.

TABLE I

Charcoal Data (Charge 35)

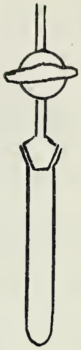
Charcoal Sample No.	Volume Activity	Hgdensity
1	1.5	1.140
2	3.8	1.103
3	6.2	1.086
4	11.4	1.036
5	11.6	1.034
6	17.3	0.969
7	21.7	0.933

Procedure

Charcoal Weights: -

The true weights of the charcoals were determined by heating each of the seven samples to 300° C

under reduced pressure in a tube as shown and noting the change in weight. This correction was applied to all samples weighed out during the experiments.



I. Adsorption from Solution

The procedure described by Lemieux and Morrison was followed with slight modifications. In general it was as follows: -

A 1 g. sample of the charcoal was weighed into a 250 ml. ground glass stoppered erlenmeyer flask. To this was added 100 ml. previously standardized acid solution and the whole was allowed to stand with frequent shaking until equilibrium was reached, as indicated by a cessation of gas evolution. Two 25 ml. samples were then taken and titrated, the difference between the normalities of the origional and final solutions giving the amount adsorbed. This procedure was repeated for each charcoal and for four to five concentrations near the limit of solubility of the adsorbate. Thus several points on the upper, saturated portion

of the Langmuir isotherm were obtained. The average of these gives the maximum amount of acid adsorbed.

Due to the great solubility of malonic, glutaric and maleic acids, smaller amounts of solution and larger samples of charcoal had to be used. Here 25 ml. portions of acid solutions were added to 4 g. of charcoals 1, 2,3 and 4, and 3 g. of 5, 6 and 7 in 50 ml. erlenmeyers. These were corked and allowed to stand for 7 to 8 days until gas evolution ceased and two 10 ml. samples were taken and titrated. As before, four or five points were determined and averaged.

These two methods were compared using succinic acid and were found to agree within experimental errors.

The time to saturate two of the charcoals with various adsorbates was determined. This was accomplished by using seven erlenmeyers containing 1 g. samples and 100 ml. of solution. The time of immersion of the charcoal was noted and the erlenmeyers were sampled, one at each interval of 1/2, 1, 2, 4, 8, 16 and 24 hours. This procedure was followed for the normal fatty acids on charcoals 3 and 7.

II. Adsorption of Butane and Nitrogen

For this work it was necessary to construct an apparatus similar to that described by Emmett (10) and others. This apparatus used is shown diagramatically in figure 1 and in the photograph.

The essential parts with reference to figure 1 are: an adsorption bulb A, a calibrated gas burette B with water jacket, a manometer M, a Mc Leod gage G (to ascertain the order of magnitude of the vacuum), bulbs for storage of gases H, I, J and, finally, a diffusion pump D backed by an oil pump (not shown). Mercury is raised or lowered in G, B and M by pressure or suction in mercury reservoirs R, S and T.

The gases used were allowed to enter the evacuated bulbs through purifying traps. For nitrogen, the trap was immersed in liquid air, for butane, the trap was immersed in an ice bath and for helium, the trap contained charcoal and was immersed in liquid air. The pressures of the stored gases were measured by manometers N, O and P.

At the beginning of an experiment, a bulb containing 0.2 to 0.25 g. of the charcoal was fused to the system. Adsorbed water and gases were re-

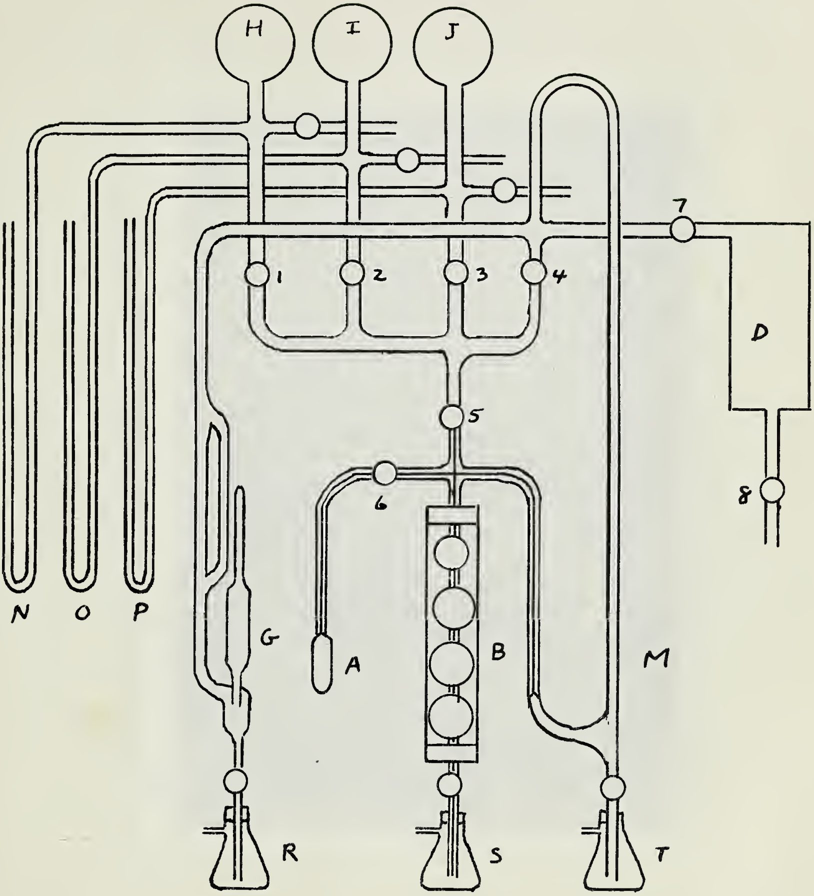
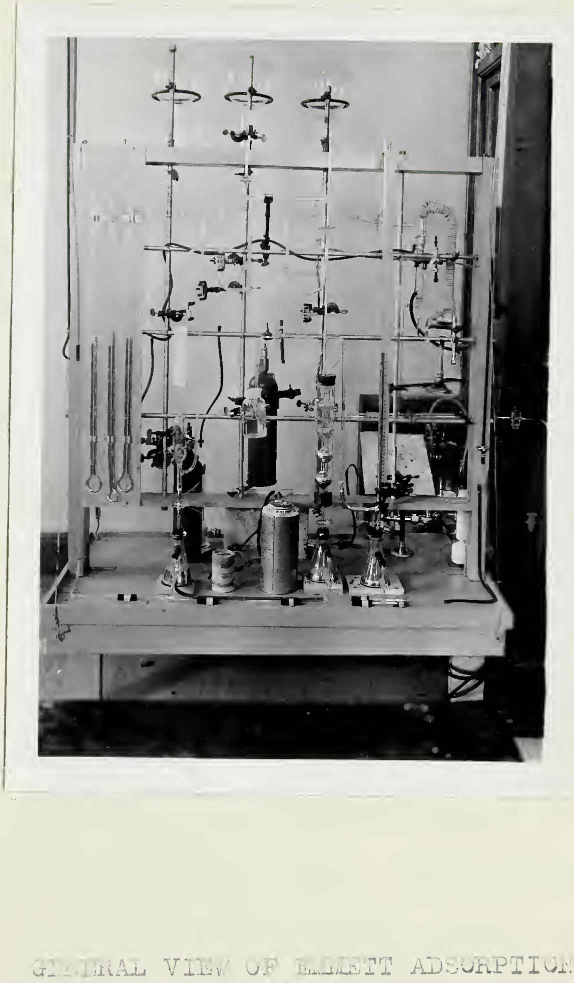


Fig. 1. Emmett Adsorption Apparatus



GENERAL VIEW OF EMMETT ADSORPTION
APPARATUS

moved by heating to 300° C for one hour under vacuum.

When this was complete the sample was cooled, stopcocks 4, 6 and 7 were closed and pumping stopped. The mercury was raised in M and an amount of helium was allowed to enter B through stopcocks 3 and 5. The volume and pressure were noted and, with 5 closed, 6 was opened. From the new reading of the manometer M, the dead space around the charcoal in A was determined, since the adsorption of helium is negligible.

The system was again evacuated and, after immersing A in liquid air, a sample of nitrogen was taken, similar to helium, and allowed to expand into A. The difference in the pressure drops of nitrogen, as compared with helium, gave the amount of adsorption of nitrogen. Successive samples of nitrogen were admitted to the burette and then to the adsorption bulb to give the adsorption for different pressures. The same procedure was followed in making adsorption measurements with butane after replacing the liquid air bath by an ice water bath. The nitrogen was desorbed by heating and evacuation prior to the butane adsorption.

In calculating the amounts of adsorption of these gases all volumes were referred to S.T.P. The amount of adsorption (Va), then, was simply: -

$$V_a = V_B + V_D - V_b - V_d$$

where: V_B = gas volume in burette before adsorption,

V_D = amount of residual gas in dead space following previous adsorption,

V_b = amount of gas in burette following adsorption

V_d = amount of gas in adsorption bulb following adsorption.

The values of V_D and V_d had to be corrected for the imperfection of the gases. These are as follows: -

N_2, + 5% at 80° K

$N\text{-}C_4H$, + 10.8% at 273° K

RESULTS

RESULTS

The maximum number of millimoles of acid adsorbed are given in table IV. These include the acids determined by Lemieux and Morrison to provide a more complete picture.

The equilibrium times for the adsorption of acids from solution were measured on charcoals 3 and 7 and are given in table II

TABLE II

Equilibrium Times of Adsorption from Solution on Charcoals

Adsorbate	Charcoal 3	Charcoal 7
Acetic Acid	16 hours	4 hours
Propionic Acid	16 hours	4 hours
Butyric Acid	10 hours	6 hours
Valeric Acid	8 hours	10 hours
Caproic Acid	4 hours	16 hours

For the adsorption of butane and nitrogen, the adsorption isotherms are shown in figures 2 and 3. Since all the curves follow the Langmuir with the exception of nitrogen on charcoal 1, the maximum adsorp-

tion was obtained by plotting P/V against P, the slope of the line giving 1/vm, where vm is the maximum volume adsorbed. The value of vm for nitrogen on charcoal 1 was found in the same way but only the points on the section of the curve following Langmuir's equation were used. These graphs are shown in figures 4 and 5, and the values for vm are given in table III.

TABLE III

Maximum Adsorption of Gases in Millimoles per Gram of Charcoal

Adsorbate	Charcoal Number						
	1	2	3	4	5	6	7
N-Butane	0.95	2.03	2.38	3.68	3.93	4.14	4.64
Nitrogen	4.80	6.38	7.59	10.0	11.1	11.8	14.6

Duplicate runs were made on certain of the charcoals and were found to be in satisfactory agreement.

TABLE IV

MAXIMUM NUMBER OF MILLIMOLES ACID ADSORBED PER GRAM CHARCOAL

Acid Adsorbate	Charcoal Number						
	1	2	3	4	5	6	7
Acetic	2.15	2.55	2.85	3.22	3.25	3.70	4.00
Propionic	1.63	2.04	2.47	2.91	2.93	3.46	3.75
Butyric	1.24	1.66	2.06	2.63	2.74	3.43	3.84
Valeric	0.88	1.31	1.75	2.40	2.41	3.18	3.66
Caproic	0.75	1.10	1.32	1.96	2.04	2.63	3.00
Isobutyric	0.70	1.20	1.60	2.50	2.64	3.20	3.50
Isovaleric	0.55	0.97	1.24	1.85	2.18	3.01	3.14
Trimethyl-Acetic	0.37	0.75	1.00	1.58	1.85	2.65	2.90
Crotonic	1.10	1.61	2.10	2.70	2.79	3.40	3.95
Oxalic	1.27	1.56	1.74	2.00	2.15	2.40	2.54
Malonic	0.60	0.78	1.09	1.40	1.52	1.62	1.87
Succinic	0.61	0.91	1.22	1.70	1.78	2.18	2.29
Glutaric	0.23	0.42	0.82	1.10	1.15	1.49	1.69
Adipic	0.43	0.68	0.99	1.48	1.44	1.88	2.08
Fumaric	1.02	1.38	1.74	1.96	2.14	2.50	2.64
Maleic	0.67	1.02	1.32	1.70	1.71	1.98	2.18

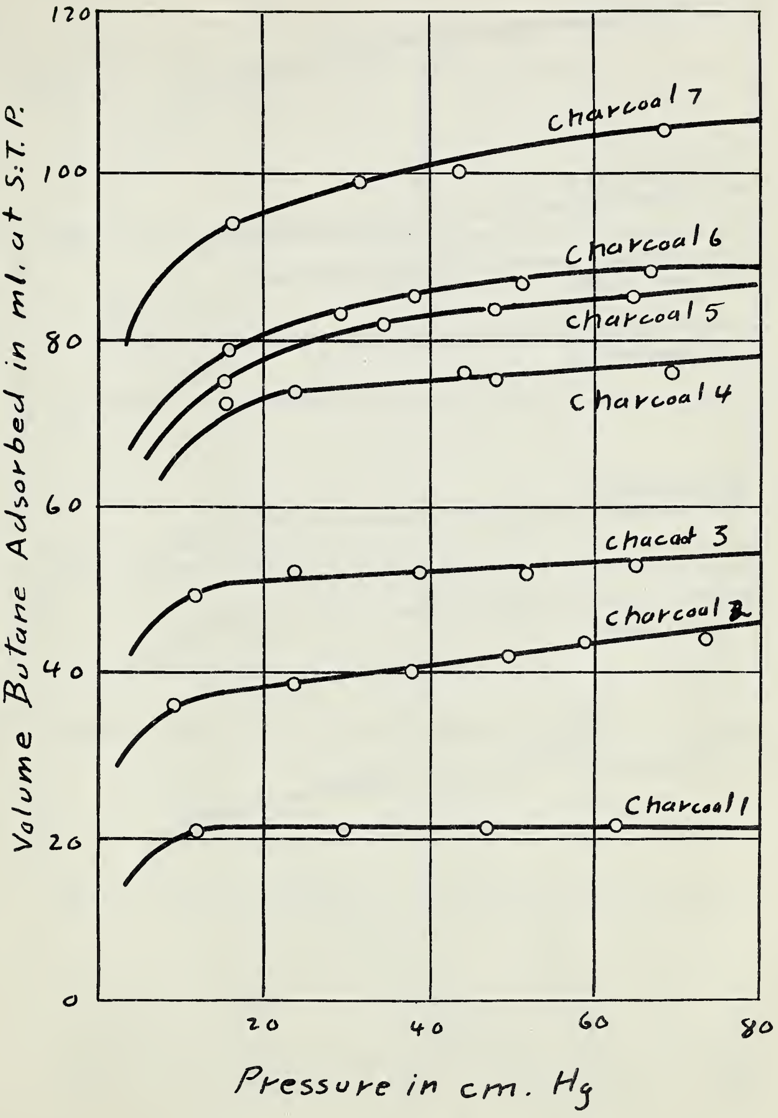


FIG. 2 - Butane Isotherms on Charge 35

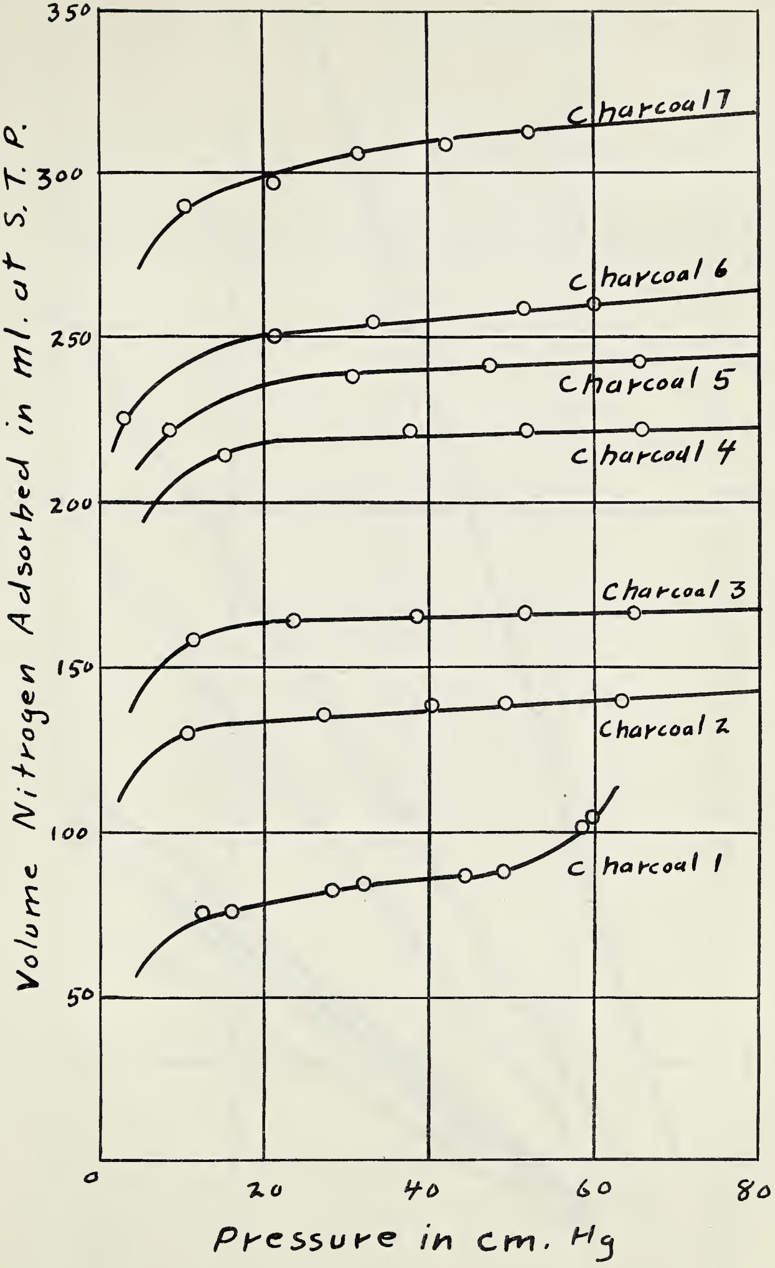


Fig. 3 - Nitrogen Isotherms on Charge 35

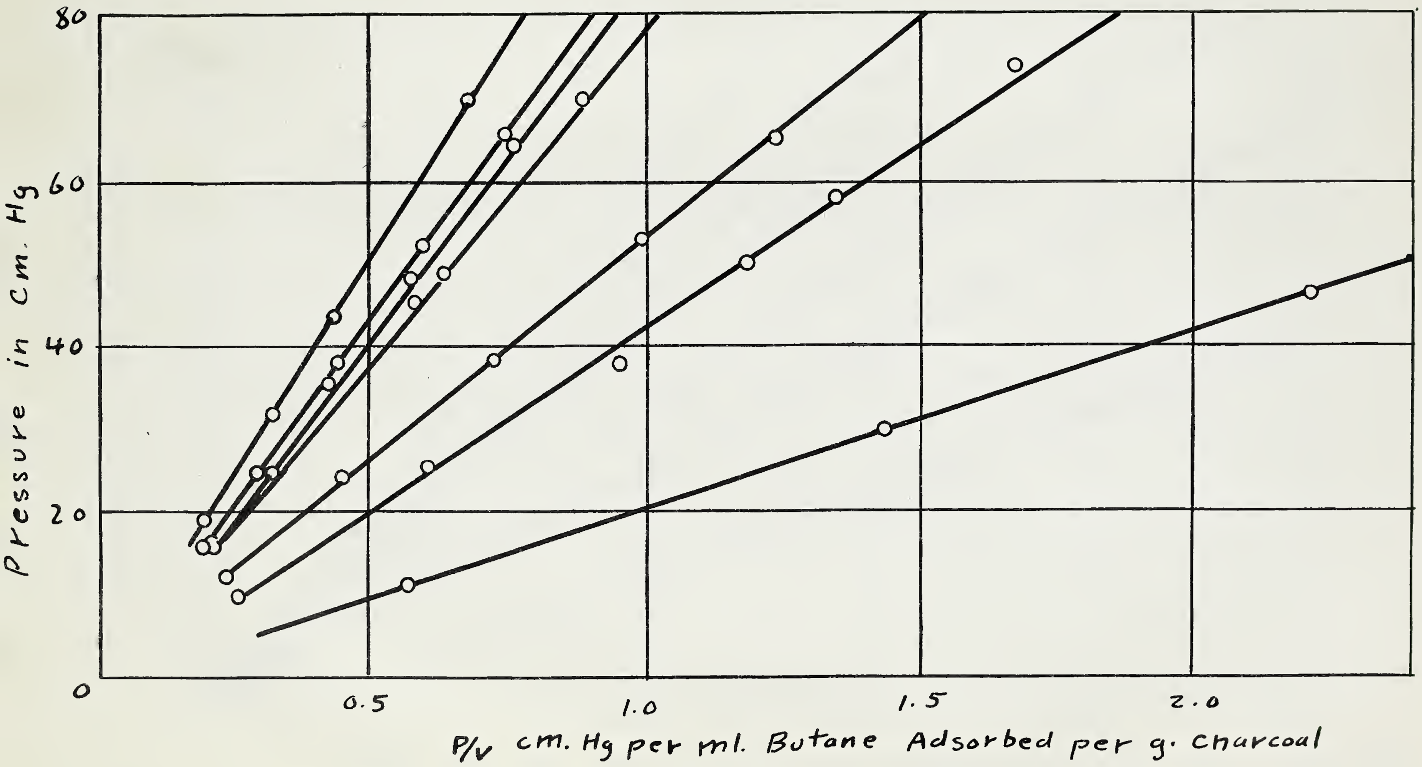


FIG. 4.- P/v versus P plot for Butane

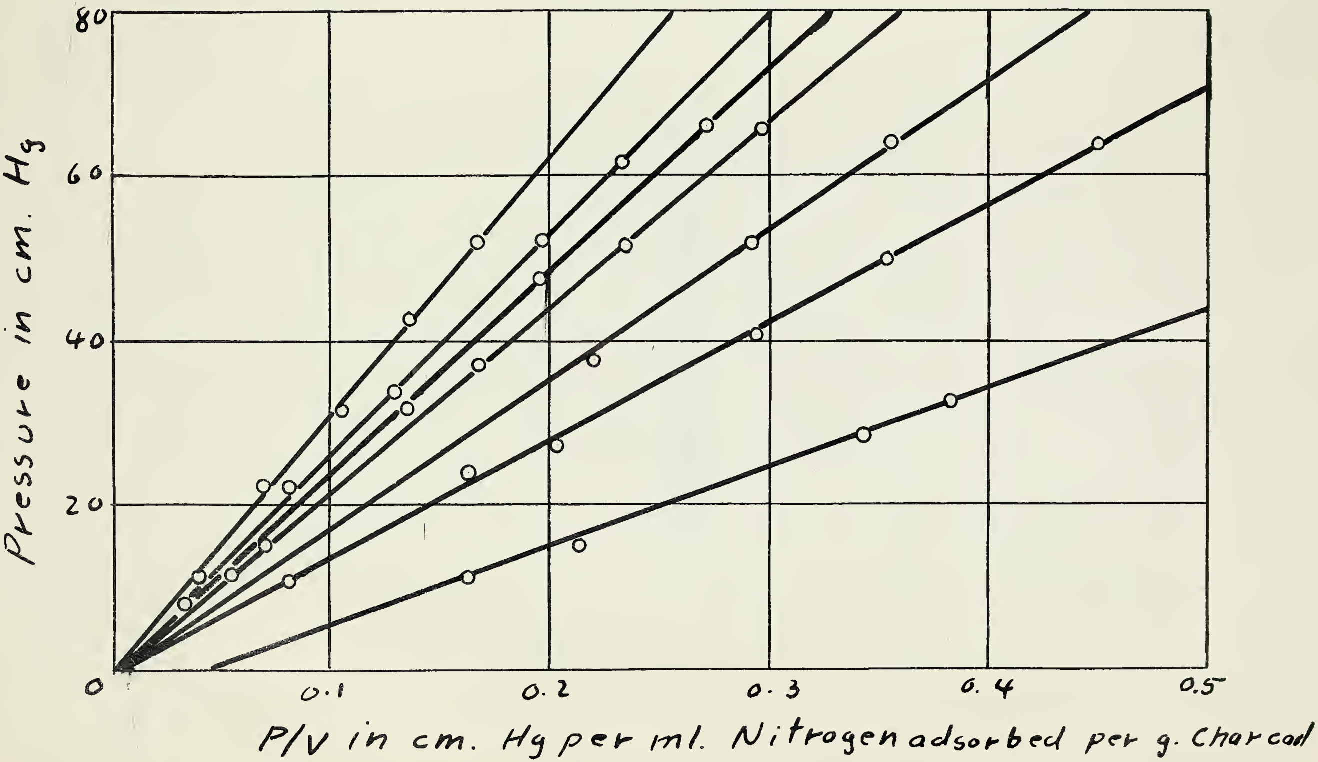


FIG. 5 - Langmuir Plot for Nitrogen on Ch. 35

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

Introduction: -

The results obtained for nitrogen and butane compared well with those obtained by Fineman, Guest and McIntosh (11) on a similar charcoal series.

Values for butyric acid on charge 35, obtained by the author, were found to be in complete agreement with those found by Lemieux and Morrison and in reasonable agreement with the results obtained by Kisselev and Shcherbakova (8) (as will be seen below). Linner and Gortner (6), also reported values of the same order of magnitude as those presented here, using the same adsorbates on norite decolorising charcoal.

It must be appreciated, however, that complete agreement is impossible between two different charcoals since the structure of any charcoal depends on its history. In fact, variations were found to occur between samples taken from different parts of the same charge at the same time.

Orientation and Unimolecularity

Kisselev and Shcherbakova worked with a single charcoal. They found the volume adsorbed for various

substances from water solutions. In every case (except acetic and propionic acids) these volumes were the same. This led them to the conclusion that adsorption is accompanied by a filling of the micropores by solute forced out of solution. The absence of any screening effect is implicit in this interpretation.

Lemieux and Morrison on the other hand interpreted their results as indicating unimolecularity of the adsorption layer.

Let us now attempt to explain the results of Lemieux and Morrison on the basis of the interpretation of Kisselev and Shcherbakova. This is facilitated by plotting the volume adsorbed against the volume activity* (figure 6). In the absence of a screening effect, the volume adsorbed would be the same for all acids on any one charcoal. Obviously this is not the case and the volume adsorbed is seen to increase with the size of the molecules. Thus this interpretation is not applicable

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* Volume activity is an empirical routine test of the retentivity of CCl_4. It is an approximate measure of the pore volumes accessible to CCl_4.

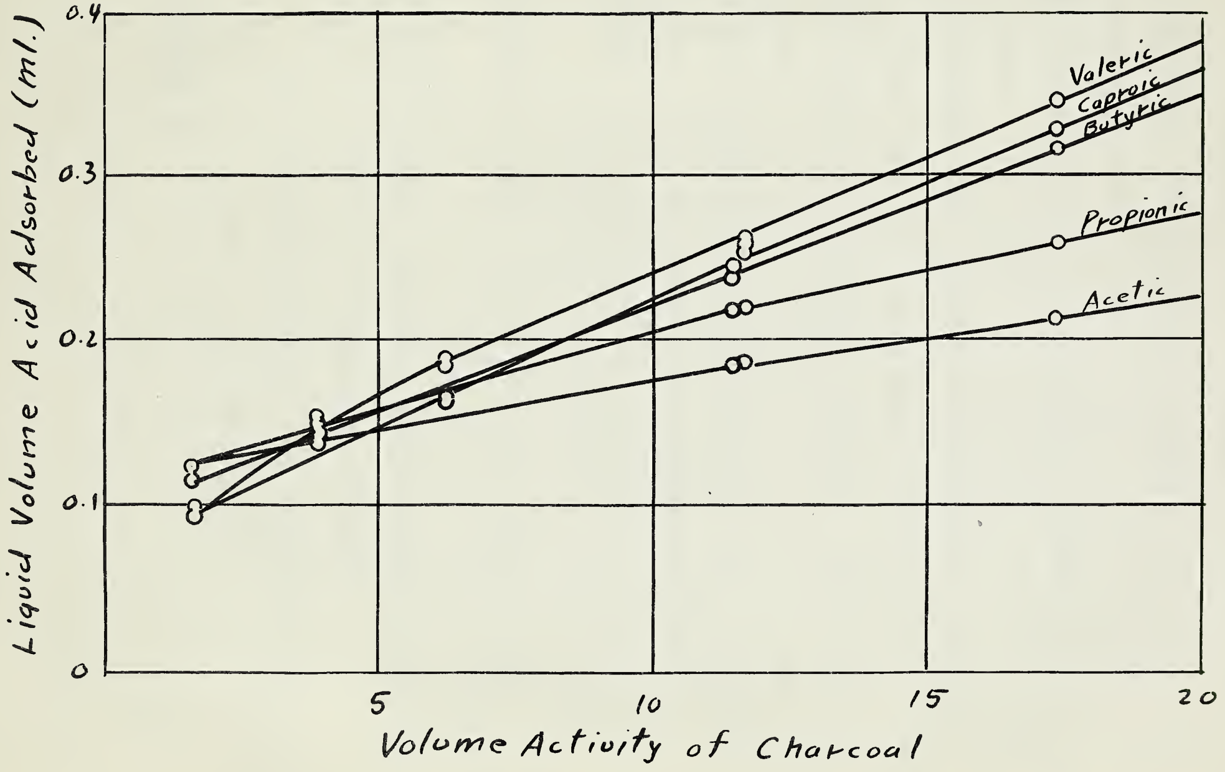


Fig. 6 - Volume Acid Adsorbed against Volume Activity

to all charcoals.

A combination of screening effect and oriented unimolecular adsorption as proposed by Lemieux and Morrison, however, accounts for these results. At lower activations, the adsorbed volumes of the larger molecules are reduced by screening. At the higher activations, the numbers of millimoles adsorbed of all acids approach each other but the volumes increase as the molecular lengths increase. This would be expected if the orientation were in such a way that the area occupied by each molecule were the same. In this case an increase in length produces an increase in the volume of the adsorbed layer.

In figure 6, the volume of caproic acid adsorbed is seen to be less than valeric acid. This is probably due to an exclusion of caproic acid from the small pores, an effect which would be expected to appear at sufficient molecular length.

The results Kisselev and Shcherbakova obtained on their charcoal are similar to those for charcoal 5 (table V)

TABLE V

Millimoles Fatty Acids Adsorbed by Charcoal 5 (Charge 35) and the Charcoal of Kisselev and Shcherbakova

Acid Adsorbate	Charcoal 5 (Charge 35)	K. and S. Charcoal
Acetic	3.25	3.24
Propionic	2.93	3.17
Butyric	2.74	3.20
Valeric	2.41	2.59
Caproic	2.04	2.24

Again this is evident in figure 6 where charcoal 5 is seen to adsorb approximately the same volume of butyric, valeric and caproic acids, but smaller volumes of acetic and propionic acids. This was also found by Kisselev and Shcherbakova to be the case with their charcoal. It is probable, therefore, that in the case of these two charcoals, the screening effect counteracts the difference in volume adsorbed which would otherwise appear as a result of increase in molecular length. For these two charcoals, both interpretations are equally valid. For charcoals of higher activation, however, the interpretation of Kisselev and Shcherbakova would not apply.

Adsorption Areas - The area accessible to the adsor-

bates in each charcoal can be computed by multiplying the number of molecules adsorbed by the area occupied at the interface by one molecule. These latter values, calculated from Szyszkowski's measurements (Rideal (12)), are 24.3± 0.3Å^2, for the normal fatty acids and 25.1Å^2 for isovaleric and isobutyric acids at the solution - air interface. The same values were found for the aqueous solution - benzene interface, and so may be considered applicable to the solution charcoal interface.

Using these values the areas of the charcoal series are calculated and are given in table VI.

TABLE VI

Charcoal Areas (in m.^{2} per g.) for Acid Adsorbates on Charge 35

Acid Adsorbate	Charcoal Number						
	1	2	3	4	5	6	7
Acetic	316	375	419	474	478	544	589
Propionic	240	300	363	428	431	509	551
Butyric	182	244	303	387	403	505	565
Valeric	128	193	258	353	354	468	538
Caproic	109	162	194	288	300	387	441
Isobutyric	107	183	244	381	402	487	533
Isovaleric	76	148	189	281	332	459	478

Activation

During the initial stages of the activation of charcoal, probably a large number of small pores are formed by oxidation along the cellulose fibers. As activation progresses, the average pore would increase in size and become more accessible to all sizes of molecules. This is indicated by the fact that charcoal areas of all molecules approach each other (table VI)

An indication of this increase in pore size is also given by the times for penetration of the acid solutions. If we consider that the slow process in adsorption is the rate of migration of the molecules into the micropores, and is dependent on the size of the molecule relative to the pore size, we may interpret the results of table II in the following manner.

The average pore of charcoal 3 is small enough to exclude the longer molecules, but large enough to allow the shorter molecules to diffuse slowly into them. Here screening is the important effect. The average pore of charcoal 7, on the other hand, allows the entry of all the molecules and the equilibrium times depend on the rate of diffusion of the different sized molecules.

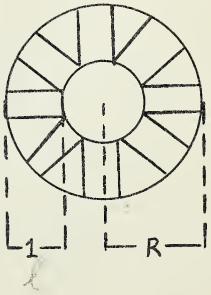
Further activation has been shown by Trost and Morrison (7) to result in a decrease in area due to breaking down of pore walls.

Pore Sizes and Molecular Orientation

An attempt will now be made to calculate the average pore radius of the various charcoals, based on the areas as given in table VI, and the lengths of the adsorbate molecules. The latter values are computed from the molal volumes and the crossectional area per molecule. These values are:

Acetic	3.9 Å
Propionic	5.1 Å
Butyric	6.2 Å
Valeric	7.4 Å
Caproic	8.5 Å

To find the relationship between area, radius and length of molecule, consider a cylindrical pore of radius R as shown. The acid molecule, of length 1, is oriented in such a way that the carboxyl group is in the polar solvent, water. The compactness of the film can be seen to depend on the size of the carboxyl group. The area these groups occupy is the area of



of a cylinder of radius (R - l) or

$$A = 2\pi h(R-1) \qquad (1)$$

Differentiating A with respect to l gives:

$$\frac{dA}{d1} = -2\pi h$$

or

$$h = -\frac{1}{2\pi}\frac{dA}{d1}$$

Substituting this value of h in (1) we get an expression for R:

$$R = -A \Big/ \frac{dA}{d1} + 1$$

The values of dA/dl can be found from the graphs of the area for each adsorbate on each adsorbate molecule. These curves for the fatty acids are given in figure 7 and the values of R, calculated from them, are given in Table VII.

TABLE VII

Average Pore Radii for Charcoals of Charge 35

Acid Adsorbate	(LENGTH) 1	Values of R in Å for Charcoals 1	2	3	4	5	6	7
Acetic	3.9	8.9	9.9	12.5	15.7	15.9	22.6	22.3
Propionic	5.1	10.0	11.3	12.5	15.8	15.9	35.1	10.6
Butyric	6.2	9.9	11.4	12.4	15.6	16.3	34.2	100.4
Valeric	7.4	10.0	11.5	12.7	16.2	16.3	16.4	64.0
Caproic	8.5	14.7	14.3	12.5	15.7	16.0	13.7	93.8
Average		10.0	11.4	12.5	15.7	16.1	------	----

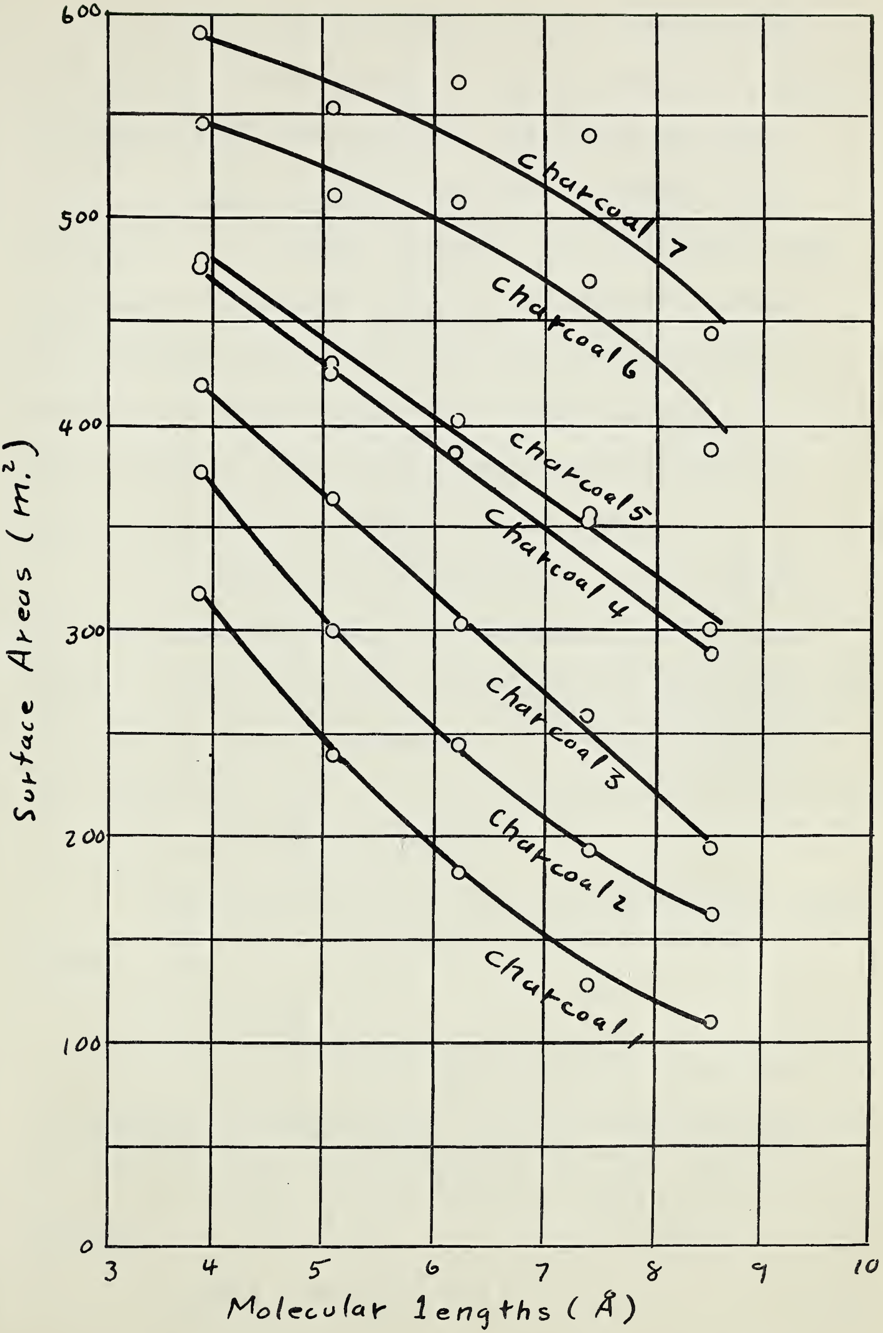


Fig. 7- Surface Areas Vs Lengths

No constant values for the average pore radii of charcoals 6 and 7 can be obtained since, as has already been stated, the pores are probably no longer regular in shape or size. The values of the others, however, are in fairly good agreement with those obtained by Fineman, Guest and McIntosh (11), who found the average pore size for a similar charcoal series to be 11 Å. These workers used the Kelvin equation and the water isotherms to obtain this value.

It should now be possible, on the basis of these calculations, to determine the orientation of other adsorbate molecules by calculating the values of l (the thickness of the adsorbed layer) and comparing these to the dimensions of the molecules This may be done as follows:

Equation (1) gives the area of the adsorbed layer; also

$$A = m N s$$

where m is the number of moles adsorbed, N is Avogadro's number and s is the area presented at the interface by the adsorbed molecule. Equation (1) becomes

$$mNs = 2\pi h(R-l) \qquad (2)$$

Since m and R are known, the value of dm/dR can be evaluated from a graph. Thus by differentiation we get:

$$\frac{dm}{dR} = \frac{2\pi h}{Ns}$$

or

$$h = \frac{Ns}{2\pi} \cdot \frac{dm}{dR}$$

and by substituting this value for h in (2) we arrive at the value for l:

$$l = R - m/\frac{dm}{dr}$$

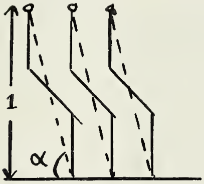
This equation may be tested by determining the value of l for isobutyric and isovaleric acids and comparing these to the values calculated from the molar volumes.

The length of isovaleric acid, as found from this equation, is 7.3 Å. From liquid density it is 7.1Å, which is within 3%.

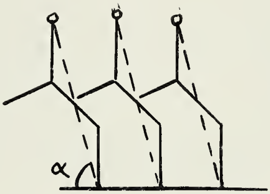
Isobutyric acid, however, shows a marked difference with 7.0Å from the equation and 6.1Å from the liquid density. This disagreement may indicate a difference in orientation between the normal and isovaleric acids on the one hand and isobutyric on the other.

X-ray studies made by Müller (13) on the

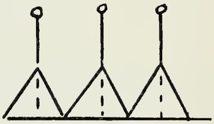
normal fatty acids have shown that the acid chains are at an angle to the crystal face in the solid state. Since this allows for better packing, it might be expected to occur at the interface also, thus: -



butyric



Isovaleric



Isobutyric

No tilting is possible in the case of isobutyric acid.

It now becomes necessary to recalculate the values for R, based on a more accurate value for l, obtained from the expression

$$l = L \sin\alpha$$

where L = length of molecule from liquid density,

and α = approximately 60°. The revised values of l will be:

propionic	4.4 Å
butyric	5.4 Å
valeric	6.4 Å
caproic	7.4 Å

Acetic remains the same since it possesses no

hydrocarbon chain.

A new evaluation of R for the first five charcoals gives the following results:

Charcoal 1	9.0 Å
Charcoal 2	10.5 Å
Charcoal 3	11.6 Å
Charcoal 4	14.9 Å
Charcoal 5	15.5 Å

Finally, a recalculation of l for isobutyric and isovaleric acids give 6.4 Å for isobutyric, a 5% agreement with L, and 6.6 Å for isovaleric, a 7% agreement with the L sin α value.

Orientation of the Dicarboxylic Acids

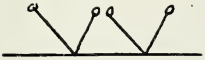
When applied to the dicarboxylic acids, the above treatment yields the following values for l:

Malonic acid	5.5 Å
Succinic acid	6.3 Å
Glutaric acid	7.5 Å
Adipic acid	5.0 Å
Fumaric acid	2.5 Å
Maleic acid	4.3 Å

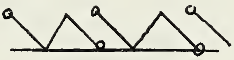
Oxalic acid gives a negative value so is omitted. No explanation can be offered for the low value for fumaric acid but it is probable that it

is oriented with the plane of the carbon atoms parallel to the charcoal plane. This is probably true for maleic acid also.

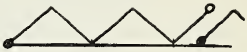
Malonic, succinic and adipic acids appear to be oriented horizontally to the charcoal surface with the plane of the carbon atoms perpendicular to this surface in this manner:



Malonic



Succinic



Adipic

This type of film should satisfy the second criteria offered by Garner, McKie and Knight (4), since the forces causing association in the solid state are still able to operate here, although weakened by the dielectric effect of water.

Glutaric acid appears to be oriented perpendicular to the surface. Possibly this position permits tighter packing.

Nitrogen Areas

The molar volume of liquid nitrogen is 34.6 ml. That for water is 18 ml., while the smallest molar volume of the acid adsorbates is 57.3 ml. (acetic acid). It is probable that the screening effect is a function of the molar volume of the adsorbate. It is unlikely that water would restrict the penetrability of the acids.

The adsorption area chosen for the nitrogen molecule is 13.8 $\mathring{A}^2$. This was found by Gaudin and Bowdish (14) for nitrogen adsorbed on glass spheres. The areas calculated from this value are given in table VIII.

TABLE VIII

Adsorption Areas of Nitrogen on Charge 35

Charcoal No.	1	2	3	4	5	6	7
Millimoles	4.80	6.38	7.59	10.0	11.1	11.8	14.6
Area in m^2.	401	534	635	837	930	987	1220

These areas indicate a much greater penetrability of the nitrogen molecule than the acid molecules.

Butane

The orientation of butane on a charcoal surface is generally assumed to be parallel, rather than vertical. No definite proof of this has been presented to our knowledge. A comparison of the butane adsorption with the acid adsorbates gives a clue to what this orientation might be.

The variations in the millimoles adsorbed for each acid on charcoals 1 to 5 can be attributed to two factors:

(1) the screening effect of small pores,

(2) the amount adsorbed is sensitive to the length of the acid molecules in small pores due to the nature of the packing.

However in charcoals 6 and 7, the millimoles adsorbed are similar for acetic, propionic, butyric and valeric acids. This indicates large pore size, giving equal accessibility and similar packing for these acids. It is assumed that the butane molecule reaches the same charcoal area. The area covered by the individual butane

molecule can be computed by dividing the number of butane molecules adsorbed. These values are:

on charcoal 6 - 20.1 $\mathring{A}^2$

on charcoal 7 - 20.0 $\mathring{A}^2$

Adam gives the value of 20.5 $\mathring{A}^2$ as the limiting cross-sectional area for hydrocarbon chains under zero compression.

This value of 20$\mathring{A}^2$ for butane adsorption area indicates vertical oriention. This would be expected on the theory of adsorption by induced dipole formation, which considers adsorption to be a result of interaction between surface and adsorbed dipoles. Butane has zero permanent dipole, but an induced dipole of 20.49 ml. along the long axis and 4.6 ml. ($-CH_2-$ group) along the short axis. Vertical orientation would favor greater interaction and hence greater adsorption.

In conclusion it must be noted that all calculations of area, pore radii and molecular lengths made in this work are based on the area of 24.3 $\mathring{A}^2$ for the fatty acid molecule at the solution-charcoal interface. They are therefore only as accurate as this value.

SUMMARY

SUMMARY

Using a series of charcoals ranging in activation, the adsorption from solution of caproic, isobutyric, isovaleric, trimethylacetic, crotonic, oxalic, malonic, adipic, succinic, fumaric and maleic acids were measured.

The adsorption of butane and nitrogen on the same series of charcoals was measured using an Emmett adsorption apparatus.

From the results of Lemieux and Morrison for the adsorption of acetic, propionic, butyric, and valeric acids on the same charcoal series, and the area occupied by one molecule found from Szyszkowski's measurements, the total area reached by each of these adsorbates was found.

An equation was derived giving the pore radii of the charcoals from the length of the acid adsorbates and the total adsorption areas.

From the adsorption of isobutyric acid it was found that the acid molecules were probably adsorbed at an angle to the interface. The pore radii of the charcoals were recalculated on the same basis.

The orientation of the dicarboxylic acids were estimated on the same basis.

The nitrogen adsorption areas of the charcoals were calculated using the area of the solid nitrogen molecule.

The adsorption area, and hence the orientation, of a butane molecule on a charcoal surface was estimated.

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